

# HYDROCARBON SPECIFICITY OVER CU/ZSM-5 AND CO/ZSM-5 CATALYSTS IN THE SCR OF NO

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## 1. Introduction

A large variety of catalysts has been proven to be active in the selective catalytic reduction of NO by hydrocarbons. Although O<sub>2,gas</sub> acts as a nonselective competitor for the direct combustion of hydrocarbons, the addition of O<sub>2</sub> enhances the rate of NO reduction<sup>1</sup>. This enhancement has been attributed to the oxidation of NO which leads not to NO<sub>2,gas</sub> but rather to adsorbed nitrogen oxide complexes (NO<sub>y</sub> groups).

Although the reactivity of these NO<sub>y</sub> groups has not been fully investigated, there are literature data to suggest that the hydrocarbon must first be activated. Cant and coworkers<sup>2</sup> observed a first order isotope effect when CH<sub>4</sub> and CD<sub>4</sub> were used as reductants. The authors concluded that H-abstraction was the rate limiting step for both N<sub>2</sub> and CO<sub>2</sub> formation. In general, the chemistry for the selective reduction of NO by hydrocarbons may be comparable to the chemistry of a cold flame<sup>3</sup>. For these reactions, H-abstraction is the first step in hydrocarbon activation. It is therefore plausible that the NO<sub>y</sub> groups are the sites responsible for the H-abstraction reaction<sup>4</sup>.

The role of NO<sub>y</sub> groups on Cu/ZSM-5 and Co/ZSM-5 has been investigated by FTIR spectroscopy to determine their thermal stability and reactivity towards C<sub>3</sub>H<sub>8</sub> and CH<sub>4</sub>. The nature of the evolved gases has been analyzed in separate experiments by mass spectroscopy.

## 2. Experimental

### 2.1. Catalyst preparation

Cu/ZSM-5 and Co/ZSM-5 catalysts were prepared via ion exchange at room temperature (r.t.) using a Cu(OAc)<sub>2</sub> or Co(NO<sub>3</sub>)<sub>2</sub> solution with Na/ZSM-5 (UOP lot #13023-60). Elemental analysis via inductively coupled plasma spectroscopy gave the following data: Cu/Al = 0.56, Si/Al = 18, Na/Al = 0.0; Co/Al = 0.48, Si/Al = 18, Na/Al = 0.34.

Prior to IR or MS experiments the samples were calcined for 2 hrs at 500°C in an UHP O<sub>2</sub> flow.

### 2.2. FTIR spectroscopy

Spectra were collected on a Nicolet 60SX FTIR spectrometer equipped with a liquid N<sub>2</sub> cooled detector. The samples were pressed into self-supporting wafers and mounted into a pyrex glass cell sealed with NaCl windows. Spectra were taken at r.t. accumulating 50 scans at a spectral resolution of 1cm<sup>-1</sup>. The samples could be pretreated *in situ* in a gas

flow at temperatures up to 500°C in a heating zone attached to the glass cell. After *in situ* calcination in UHP O<sub>2</sub>, as described previously, the sample was purged at r.t. for 1 hr with 25 ml min<sup>-1</sup> UHP He then saturated in a stream of NO (0.45%) and O<sub>2</sub> (75%) with a He balance. For the reduction studies the samples were heated to the reaction temperatures at 6°/min in flowing C<sub>3</sub>H<sub>8</sub> or CH<sub>4</sub> (0.25% hydrocarbon in He) at a total flow rate of 30 ml min<sup>-1</sup>. Before cooling to r.t. the sample was purged for 10 min with He. Spectra were taken at r.t.

## 2.2. MS analysis

For the analysis of released gases, 400 mg of sample were calcined *ex situ* to 500°C in UHP O<sub>2</sub> and then saturated with NO<sub>2</sub> (0.5%, balance He) at r.t. The reactor was transferred to a glass, recirculating manifold equipped with a Dycor Quadrupole Gas Analyzer. Prior to the reduction experiments the sample was heated *in vacuo* to 225°C for Cu/ZSM-5 and 150°C for Co/ZSM-5. A sample loop was then filled with a known amount of hydrocarbon; evolved gases were allowed to recirculate over the sample. The signal intensities were normalized by an Ar standard. A secondary loop to the manifold was charged with 3 g of 5 wt.% Ni/SiO<sub>2</sub> pre-reduced at 400°C. This loop was sealed from the reactor and manifold during the experiment and was used to remove CO from the post-reaction analysis of the evolved gases.

## 3. Results

### 3.1. FTIR spectroscopy

Fig. 1A shows the FTIR spectra of Cu/ZSM-5 after the exposure to NO + O<sub>2</sub> at r.t. and subsequent purge at 200°C in He. There are three distinct bands at 1628, 1594 and 1572 cm<sup>-1</sup> which are attributed to Cu<sup>2+</sup> bonded nitro and nitrate groups. These NO<sub>y</sub> groups are stable in He at 200°C for over 14 hrs. However in C<sub>3</sub>H<sub>8</sub> all band intensities decrease. A plot of the band intensities, measured as peak heights and normalized by their initial intensities, is presented in Fig1A'. The rates of reaction of the three NO<sub>y</sub> groups are different. One of the nitrate groups (1594 cm<sup>-1</sup>) reacts fast, whereas the other nitrate group (1572 cm<sup>-1</sup>) reacts sluggishly. The reactivity of the nitro group (1628 cm<sup>-1</sup>) exhibits an induction period of 20 min after which it is consumed at a comparable rate to the nitrate group at 1594 cm<sup>-1</sup>. In CH<sub>4</sub>, the Cu•NO<sub>y</sub> groups are not depleted at temperatures below the thermal decomposition.

In the case of Co/ZSM-5 the main feature after NO + O<sub>2</sub> saturation is shown in Fig 1B. It consists of two broad bands at 1526 and 1310 cm<sup>-1</sup>. The former band is ascribed to a Co<sup>2+</sup>•ONO complex. The Co•NO<sub>y</sub> adsorption complex is less stable than the Cu•NO<sub>y</sub>. Approximately 60% of the Co•NO<sub>y</sub> adsorbates are desorbed after thermal treatment at 150°C for 14 hrs. The reactivity of the remaining NO<sub>y</sub> groups with C<sub>3</sub>H<sub>8</sub> at 150°C is shown in Fig.1B'. The normalized intensities of the adsorption band at 1526 cm<sup>-1</sup> are plotted in Fig .1B' for propane and methane. Unlike Cu•NO<sub>y</sub>, Co•NO<sub>y</sub> reacts with CH<sub>4</sub>.

### 3.2. MS spectroscopy

Fig.2 shows the evolution of N<sub>2</sub> when Cu/ZMS-5 or Co/ZSM-5 samples, pre-saturated with NO<sub>2</sub>, are exposed to C<sub>3</sub>H<sub>8</sub> or CH<sub>4</sub> at reaction temperatures of 225°C for Cu/ZSM-5

and of 150°C for Co/ZSM-5. When C<sub>3</sub>H<sub>8</sub> is used as the reductant, N<sub>2</sub> evolution from Cu/ZSM-5 is rapid but terminates after 30 min exposure to hydrocarbon. N<sub>2</sub> evolution from Co/ZSM-5 proceeds at a slower rate; an increase in N<sub>2</sub> is still detected after 90 min exposure to hydrocarbon. When CH<sub>4</sub> is used as the reductant no reaction occurs over Cu/ZSM-5, but over Co/ZSM-5 N<sub>2</sub> evolution is detected. Co•NO<sub>y</sub> reaction with CH<sub>4</sub> is slower than Co•NO<sub>y</sub> reaction with C<sub>3</sub>H<sub>8</sub>.

#### 4. Discussion

NO<sub>y</sub> complexes are formed on Cu/ZSM-5 and Co/ZSM-5 after saturation with NO<sub>2</sub>. The IR spectroscopic signature, thermal stability and chemical reactivity of Cu- and Co-bonded NO<sub>y</sub> are found to be different. Cu/ZSM-5 contains not only Cu<sup>2+</sup> ions, but also [Cu-O-Cu]<sup>2+</sup> oxocations and CuO oxides. Upon interaction with NO<sub>2</sub> Cu<sup>2+</sup> ions form nitro complexes while oxocations and oxide react to nitrate complexes. On the other hand, Co/ZSM-5, which contains only Co<sup>2+</sup> ions, can only form NO<sub>2</sub> complexes. Unlike Cu<sup>2+</sup>•NO<sub>2</sub>, these are most likely Co<sup>2+</sup>•ONO nitrito complexes.

Although deNO<sub>x</sub> catalysis over both Co/ZSM-5 and Cu/ZSM-5 may be initiated in the same manner, H-abstraction, the two display a different hydrocarbon specificity; Cu/ZSM-5 requires C<sub>2</sub>+ olefins or C<sub>3</sub>+ paraffins, whereas Co/ZSM-5 is active with CH<sub>4</sub> and higher hydrocarbons. The type of the NO<sub>y</sub> groups differs which may explain the differences in hydrocarbon specificity.

Assuming that the activation of hydrocarbon occurs via an H-abstraction as stated by others<sup>3,4</sup>, this reaction is affected by NO<sub>y</sub> groups. While exposure to C<sub>3</sub>H<sub>8</sub> leads to N<sub>2</sub> formation from both samples, only Co/ZSM-5 formed N<sub>2</sub> upon CH<sub>4</sub> exposure. It appears that H-abstraction from CH<sub>4</sub> is difficult with Cu•NO<sub>y</sub> but facile with Co•NO<sub>y</sub>. The influence of the metal ion on the selectivity in NO reduction may be indirect by furnishing different types of NO<sub>y</sub>.

The fate of the hydrocarbon radical is not yet clear. It has been proposed that a reactive intermediate containing at least one carbon, nitrogen and oxygen atom is formed on the catalyst surface which reacts further with NO to form N<sub>2</sub>. The role of NO<sub>gas</sub> and the nature of the reactive intermediate are currently under investigation.

#### 5. Acknowledgments

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<sup>1</sup> M. Iwamoto, Proc. of the Meeting of Catalysis Technology for the Removal of Nitrogen Monoxide, Tokyo, Japan (1990) 17.

<sup>2</sup> A.D. Cowan, R. Dümpelmann and N. W. Cant, J. Catal., 151 (1995) 356.

<sup>3</sup> F. Witzel, G.A. Sill and W.K. Hall, J. Catal., 149 (1994) 229.

<sup>4</sup> Y. Li, T.L. Slager and J.N. Armor, J. Catal., 150 (1994) 388.

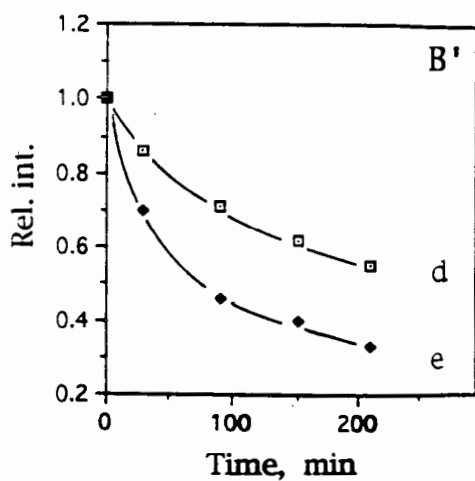
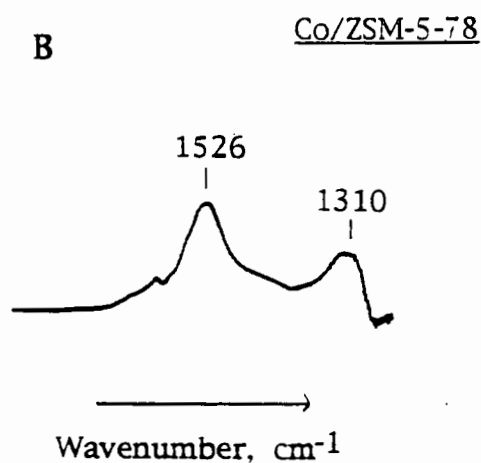
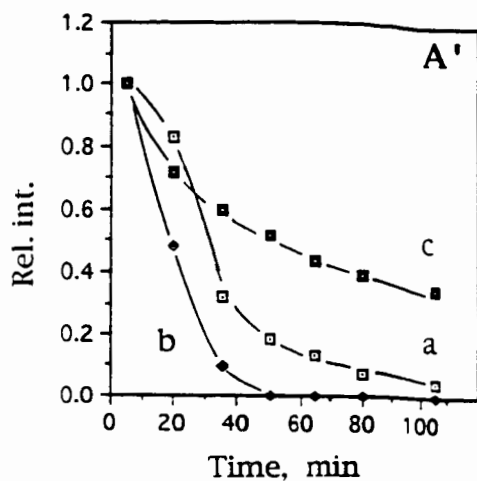
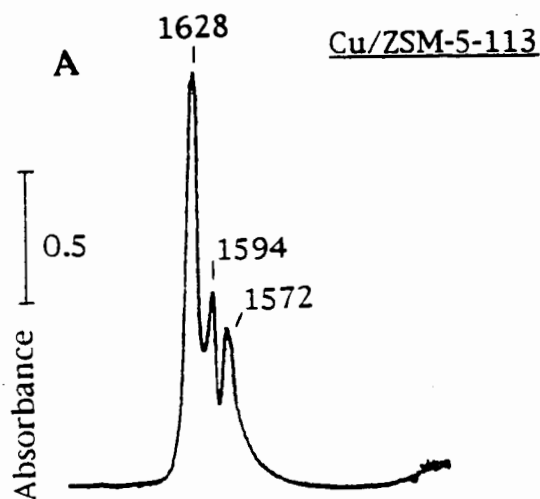


Fig.1: FTIR spectra of Cu/ZSM-5 (A) and Co/ZSM-5 (B) after calcination, exposure to  $\text{NO} + \text{O}_2$  at r.t. and He purge at 200°C (A) and 150 °C (B). Graph A', the relative intensities of  $\text{NO}_y$  bands at 1628  $\text{cm}^{-1}$  (a), 1594  $\text{cm}^{-1}$  (b) and 1572  $\text{cm}^{-1}$  (c) in 0.25 % propane at 200 °C vs. time. Graph B', the relative intensities of  $\text{NO}_y$  band at 1526  $\text{cm}^{-1}$  in 0.25 % methane (d) and 0.25 % propane (e) at 150 °C vs. time.

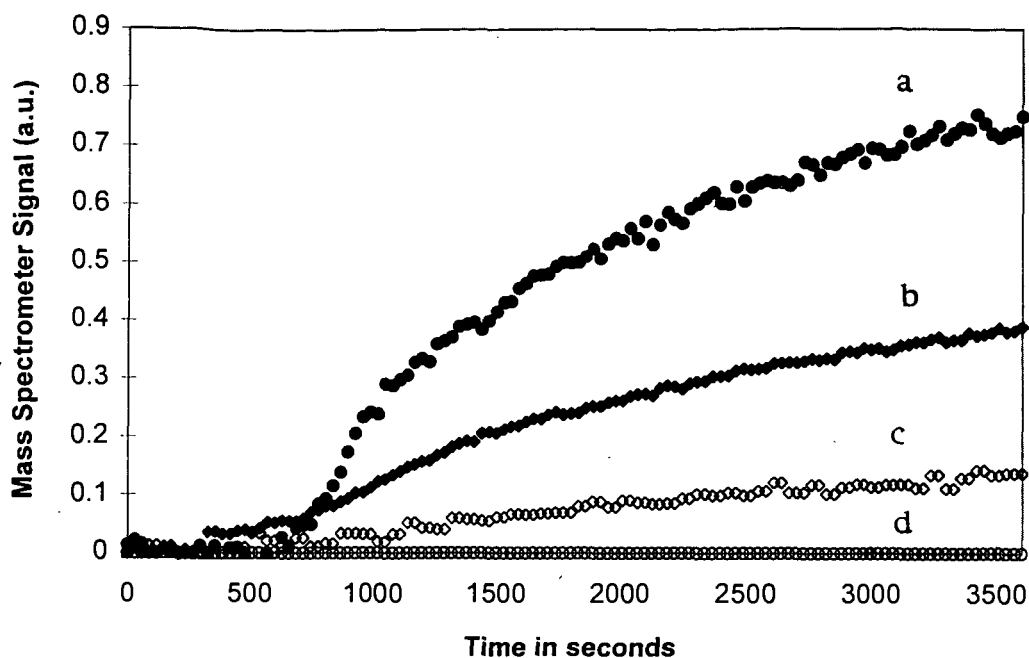


Fig.2:  $N_2$  evolution from Co/ZSM-5 at 150°C (b, c) and Cu/ZSM-5 at 225°C (a, d) upon interaction with  $CH_4$  (c, d) and with propane (a, b) vs. time. Samples have been calcined, saturated with  $NO_2$  at r. t. and outgassed at the respective reaction temperature prior to reaction.